Host–Guest Systems

Technetium-99 MAS NMR Spectroscopy of a Cationic Framework Material that Traps TcO$_4^-$ Ions**

Ping Yu, Shuao Wang, Evgeny V. Alekseev, Wulf Depmeier, David T. Hobbs, Thomas E. Albrecht-Schmitt,* Brian L. Phillips,* and William H. Casey*

The generation of energy from nuclear fission results in nonnatural isotopes such as [99]Tc. Like its congener Mn, Tc has a readily accessible +7 oxidation state that exists predominantly as the pertechnetate ion, TcO$_4^-$. However, in contrast to permanganate, the TcO$_4^-$ ion is not a strong oxidant and is relatively unreactive. Technetium is also radioactive; ^{99}Tc has a half-life of 200 000 years. The low charge and the unreactive nature of the TcO$_4^-$ ion lead to mobile behavior in the environment. The TcO$_4^-$ ion is also difficult to incorporate into vitrified waste and easily leaches away.[1] These issues have created a need for preparing new materials that are capable of sequestering the TcO$_4^-$ ion. One of these materials is the compound NDTB-1, [(ThB$_5$O$_6$(OH)$_6$)-(BO(OH)$_2$)]·2.5 H$_2$O, the extraframework borate ions of which are readily exchangeable with the TcO$_4^-$ ion.[2]

NDTB-1 possesses a porous supertetrahedral framework with building blocks of twelve-coordinate Th^{4+} ions surrounded by BO$_3$ and BO$_4$ units. Thorium atoms and B$_{10}$O$_{24}$ crownlike groups do not fill all of the space in the structure, but create a regular cationic framework with a system of channels and cavities (Figure 1) and a free-void volume of
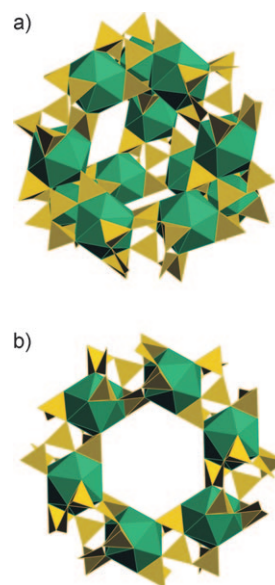
Figure 1. Fragments of the threedimensional structure of NDTB-1 (Th polyhedra green, B yellow). (a) Supertetrahedral cavity formed by the intersection of four hexagonal channels; (b) Structure of a channel. The TcO$_4^-$ ions trapped in both cavities (a) and channels (b).

43 %.[3] The channels allow for facile anionic transport, have a hexagonal form, and are 9.4 × 7.4 Å in size (Figure 1 b). Our research group has previously used solid-state ^{11}B MAS NMR experiments to confirm[2] the presence of disordered [BO(OH)$_2$]$^-$ ions in the channels, as the ions maintain charge neutrality in the cationic framework. Further questions remain concerning the location and mobility of TcO$_4^-$ ions after exchange.

Herein we report the use of ^{99}Tc MAS NMR spectroscopy to probe the behavior of the TcO$_4^-$ ions within the NDTB-1 framework. We found that the ^{99}Tc NMR signal from the exchanged material is easily observed. Figure 2 shows what we believe to be the first ^{99}Tc MAS NMR spectra reported to date,[4] which have been obtained during our characterization of the ion-exchange properties of NDTB-1. Although ^{99}Tc is quadrupolar ($I = 9/2$), the symmetry of the TcO$_4^-$ ion is

[*] S. Wang, Prof. Dr. T. E. Albrecht-Schmitt
Department of Civil Engineering and Geological Sciences and
Department of Chemistry and Biochemistry,
University of Notre Dame
Notre Dame, IN 46556 (USA)
E-mail: talbrec1@nd.edu

Dr. E. V. Alekseev, Prof. Dr. W. Depmeier
Department of Crystallography, University of Kiel
24118 Kiel (Germany)

Dr. D. T. Hobbs
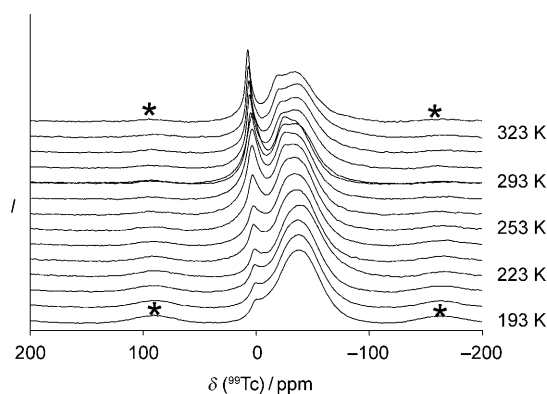Savannah River National Laboratory, Aiken, SC 29808 (USA)

Dr. P. Yu
University of California, Davis, CA 95616 (USA)

Prof. Dr. W. H. Casey
Department of Chemistry, Department of Geology,
University of California, Davis
One Shields Ave, Davis, CA 95616 (USA)
E-mail: whcasey@ucdavis.edu

Prof. Dr. B. L. Phillips
Department of Geosciences, SUNY-Stony Brook
Stony Brook, NY 11794-2100 (USA)
E-mail: brian.phillips@sunysb.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002646.

Figure 2. Variable-temperature (VT), and solid-state ^{99}Tc MAS-NMR spectra of NDTB-1 that had been exchanged with TcO_4^- ions in solution to replace the extraframework BO_4^- ions. Two signals are evident: a narrow signal near 0 ppm and a broader signal centered near −40 ppm. There is also evidence of a third signal on the broader peak at 293 K to 323 K. The overlapping spectra at 293 K are repeated during the VT series to examine hysteresis, which is small. Asterisks denote the positions of spinning sidebands. Chemical shift values are reported relative to free TcO_4^- ions.

sufficiently high that the quadrupolar broadening is limited and the aqueous TcO_4^- ion exhibits an inherent peak width of approximately 3 Hz in solution.[4] The ^{99}Tc MAS NMR spectra of TcO_4^--exchanged NDTB-1 show the presence of at least two sites where TcO_4^- ions reside in the material (Figure 2).

The two most conspicuous signals in the ^{99}Tc MAS NMR spectrum are a narrow peak near 0 ppm, with approximately 1.5 kHz full-width at half-maximum (fwhm) at 293 K, and a broader peak centered near −40 ppm, with approximately 4.6 kHz fwhm at 293 K. The intensity of the sharp, narrow peak (Figure 2) diminishes markedly with decreasing temperature, consistent with its assignment to TcO_4^- ions (Figure 2) that undergo rapid, near-isotropic tumbling near room temperature. This motion slows down when the temperature decreases, and produces resolved signal only from the central transition at 193 K. With increasing temperature this signal moves slightly downfield (to $\delta = +8$ ppm at 323 K) and becomes slightly more separated from the upfield signal, thus indicating absence of spectroscopic effects that result from any chemical exchange between the two TcO_4^- environments.

At all temperatures, the broader upfield signal is accompanied by sets of spinning sidebands (Figure 2). At 223 K, the signal can be modeled with a broadened second-order central-transition quadrupolar lineshape, but is not well-constrained. The absence of a quadrupolar fine-structure indicates the presence of a range of local environments, as was also found for the extraframework boron atoms prior to ion exchange.[2] The NMR spectra are consistent with the interpretation that the chemical environment around the ^{99}Tc nucleus is disturbed by the interaction with the cationic framework. Furthermore, the width of the ^{99}Tc NMR signal and the intensity of the spinning sidebands support the assignment to a dynamically rigid species, in contrast to the narrow downfield signal, where the experimental evidence suggests ion mobility. The ^{99}Tc nutation experiments are

consistent with this interpretation—the broad signal exhibits complex nutation with an apparent π/2 pulse width that is 2–3 times shorter than that for the narrow signal, suggesting that only the ^{99}Tc nuclei represented by the broad signal experience a significant quadrupolar interaction.

The smaller signal contains about $(6 \pm 1.5)\%$ of the total intensity at 193 K. The reduction in intensity of this narrow signal with temperature indicates that all the ^{99}Tc transitions are dynamically averaged into a narrow signal at room temperature. When the sample cools, the dynamic averaging diminishes, thus causing the signals, which correspond to the satellite transitions, to be broadened into the baseline, therefore leaving only the central transition.

An additional signal that resembles fine structure from second-order quadrupolar broadening is evident near −20 ppm from approximately 298 K to 323 K (Figure 2). However, the narrow feature appears to broaden with reduced temperature and has nearly the same chemical shift as the signal centered near −40 ppm, thus suggesting instead the presence of a small amount of mobile TcO_4^- ions in chemical environments (i.e., cavities) similar to those represented by the broad signal.

Although we detected no line broadening or coalescence that might indicate chemical exchange on the NMR time scale, the intensity of the narrow downfield signal grew with time over six weeks, thus suggesting slow movements between the two main sites. ^{99}Tc multiple quantum magic-angle spinning (MQMAS) experiments were attempted but the corresponding T_2 values were too short to allow the signal to accumulate. We also compared NDTB-1 samples that had been exchanged with TcO_4^- and SeO_4^{2-} ions to examine the selectivity of the cationic framework. In contrast to the ^{99}Tc-MAS NMR signals, the ^{77}Se-MAS NMR signal of NDTB-1 exchanged with SeO_4^{2-} ions produced only a single narrow signal, centered near 1045 ppm (Figure 3).
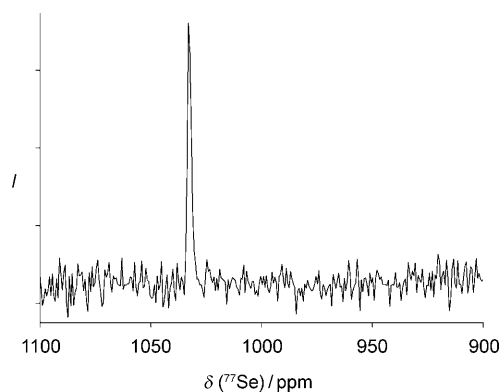
Figure 3. ^{77}Se MAS NMR spectrum of SeO_4^{2-}-loaded NDTB-1. A single narrow signal suggests that the $^{77}SeO_4^{2-}$ signal is observed only from the channels where the molecule is mobile. Chemical shift values are reported relative to free SeO_3^- ions.

The most direct interpretation of the ^{99}Tc NMR experiments is that both the channels and the cages in NDTB-1 are occupied by TcO_4^- ions, therefore the net cationic charge of the framework is balanced. We suspect that the narrow signal

near 0 ppm correspond to the TcO_4^- ions in the channels; this hypothesis is consistent with the greater space for movement available for the ions. The broader upfield signal is then assigned to the TcO_4^- ions in the cavities and accounts for most of the signal. The fact that the adsorption of SeO_4^{2-} ions gave only a single narrow signal (Figure 3) suggests that the selectivity of NDTB-1 is based upon the size-to-charge ratios of the TcO_4^- and SeO_4^{2-} ions. We speculated that stronger coulombic interactions with the framework lead to the exclusion of SeO_4^{2-} ions from the cages. It is possible, however, given the long T_1 values for ^{77}Se that the SeO_4^{2-} ions in the cavities just relaxed too slowly for us to easily detect. The ^{99}Tc NMR data show that the TcO_4^- ions in the cavities are significantly disordered, which we expected to result in a broadened ^{77}Se NMR signal.

The ^{99}Tc MAS NMR spectra show that NDTB-1 provides a cationic framework with the capacity to store the environmental contaminant TcO_4^- ion. Based on results from the ^{99}Tc and ^{77}Se NMR experiments, NDTB-1 was tested on simulated nuclear waste solutions, which contained carbonate, sulfate, chloride, nitrate, and nitrite ions in addition to the TcO_4^- ion. Despite the presence of more than 300-fold excesses of chloride and nitrate ions, and a 15-fold excess of nitrite ions in a simulated low-activity melter recycle stream, NDTB-1 selectively removed pertechnetate TcO_4^- ions with a distribution coefficient K_d of 16.2–22.9 mL g^{-1} (for TcO_4^- ions) from this solution (see the Supporting Information). This selectivity for TcO_4^- ions is unprecedented, and can be understood by the ability of NDTB-1 to trap TcO_4^- ions within the cavities in the cationic framework.

Experimental Section

The preparation of NDTB-1 is reported in reference [2]. To load the material with TcO_4^- ions, TcO_2 (50 mg) was reacted with a large excess of 30% H_2O_2 to yield a solution of TcO_4^- ions. NDTB-1 (200 mg) was added to this solution, and anion exchange was allowed to occur for seven days. This exchange process resulted in an uptake of approximately 27 mg of ^{99}Tc in the form of TcO_4^- ions into the material. Owing to the intense charge-transfer bands of aqueous TcO_4^-, we could follow its removal from the solution using UV/Vis spectroscopy. These studies showed rapid uptake of TcO_4^- ions from the solution with 70% of the ions being removed by NDTB-1 in 36 h. The solid was repeatedly washed with Millipore water, and was carefully dried at 40°C. All of the material was packed into a rotor for NMR studies. All of these procedures were conducted in a radiologic facility. A similar procedure was followed for the preparation of the SeO_4^{2-} exchanged material where the source of the selenate was a solution of Na_2SeO_4.

^{99}Tc and ^{77}Se NMR spectra were collected on a Bruker AVANCE spectrometer equipped with a widebore 11.7 Tesla magnet (operating at the resonance frequencies of 112.56 and 95.40 MHz for ^{99}Tc and ^{77}Se, respectively). A Bruker CP-MAS probe was used. The samples were loaded in a 4 mm zirconia rotor with zirconia cap in a fume hood and spun at 15 kHz. For ^{99}Tc NMR experiments we used a single, 1.3 µs nonselective pulse, 5 s relaxation delay, and a 62.5 kHz spectral window. We performed nutation experiments with relaxation delay time varying from 1 to 15 s, and found that 5 s is sufficient to prevent any signal saturation. The signal was averaged by 64 transients and processed with 200 Hz of line broadening. The chemical shift was referenced to an aqueous solution of TcO_4^- (sealed in a quartz tube) at 0 ppm.[4] For ^{77}Se NMR experiments, the pulse length was 1.7 µs (corresponding to 60 degree tip angle), the recycle delay time was 60 s, and the number of transients was 960. The chemical shift was externally referenced to a saturated aqueous solution of H_2SeO_3 at 1288 ppm.[5]

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